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Observation of giant magnetoresistance in Ce-doped $RMnO_3$ (R = La, Pr and Nd) system

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Abstract : The dc electrical resistance and magnetoresistance of Ce-doped $LaMnO_3$ are studied over a wide range of temperature from 4.2 to 300 K and in magnetic fields up to 7.7 T. In absence of any magnetic field, the temperature dependence of resistivity shows one broad and another sharp peaks near the ferromagnetic to the paramagnetic phase transition temperature. With the application of magnetic field the resistivity at the peak, (particularly the sharper one) decreases drastically, showing large negative magnetoresistance. Magnetoresistance shows a sharp peak very close to the zero field peak. The maximum value of magnetoresistance observed is 46%.

Keywords : Electrical transport, giant magnetoresistance, double-exchange

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1. Introduction

After the discovery of superconductivity in lanthanum cuprates the perovskite materials have received much interest. Observation of many interesting and new kinds of unexplained phenomena in these systems over a wide range of doping attracted the condensed matter physicists. Recent reports [1–6] of huge negative magnetoresistance (MR) termed as "giant magnetoresistance (GMR)" in other lanthanum-based perovskite stimulated further the interest in such kind of materials. Mn-based perovskites of the type $R_{1-x}A_xMnO_3$ (R is a rare-earth element and A is Ca, Ba, Sr or Pb) show very unusual transport properties with doping, temperature, with application of magnetic field and pressure, *etc* [6–8]. Above a certain critical level of doping these materials are ferromagnetic and metallic which has been explained by the spin-dependent transfer mechanism, *i.e.* the formation of a Mn^{+3} -Mn^{+4} mixed valence band [9–12]. In the doped system, the $3d$ electron in the e_g level becomes delocalised, hops among the Mn ions and couples them ferromagnetically through

the oxygen sites (double-exchange interaction). In such double-exchange (DE) systems, magnetic transition in general involves a change in the electronic structure, sometimes to the extent of metal-insulator transition, as the wave functions are very sensitive to changes in the internal polarisation. This implies that the DE model which explains the GMR effect in these perovskite materials needs the coexistance of Mn^{+3}–Mn^{+4} which is satisfied when one substitutes the trivalent rare-earth ion partially by the divalent ions in $RMnO_3$ system. On the other hand, there is no theoretical prediction for the occurrence of GMR in the mixed valence state Mn^{+2}–Mn^{+3}. Keeping the electron-doped superconductor [13] R_2CuO_4 (R = Nd, Pr, Sm) in mind we have doped the $RMnO_3$ (R = Nd, Pr, La) with tetravalent Ce ions and studied MR and other physical properties as a function of temperature [14]. These samples show very large negative MR and a ferromagnetic (FM) to paramagnetic (PM) phase transition with increasing temperature.

2. Experimental

Polycrystalline samples of nominal composition $R_{0.7}Ce_{0.3}MnO_3$ were prepared by standard solid state reaction method. Stoichiometric amounts of high purity La_2O_3 (or Pr_6O_{11}/Nd_2O_3), CeO_2 and Mn_2O_3 powders were mixed thoroughly and heated in air at temperatures 1100–1400°C for few days with intermediate grindings. The powder was then pressed into pellets and annealed in air at above temperatures for few days followed by slow cooling. As-prepared samples are slightly oxygen deficient and show larger GMR effect as compared to post-oxygenated samples. All the samples were characterised by X-ray powder diffraction with CuK_α radiation. The electrical resistivity and magnetoresistance were measured as a function of temperature by four-probe method in a superconducting magnet with maximum magnetic field up to 8 T. Magnetisation was measured using a vibrating sample magnetometer equipped with a closed cycle refrigerator.

3. Results and discussion

The X-ray diffraction patterns show that all the samples are single phase. A representative room temperature X-ray diffraction pattern of one $La_{0.7}Ce_{0.3}MnO_3$ sample is shown in Figure 1. All the diffraction lines have been assigned. The diffraction peaks are best fitted by assuming an orthorhombic unit cell with a = 5.411 Å, b = 5.525 Å and c = 7.756 Å. For the $Pr_{0.7}Ce_{0.3}MnO_3$ sample the lattice parameters are found to be a = 5.418 Å, b = 5.575 Å and c = 7.653 Å. Both the peak positions and their relative intensity for the Ce-doped samples are similar to those for the divalent-doped manganites. However, the splitting between (h,k,l) and (k,h,l) lines for the Ce-doped samples is larger than that for the divalent ion doped manganites. This indicates that in these samples the orthorhombic distortion is larger. Orthorhombic distortion decreases with increasing oxygen content. The tolerance factor which is defined as t = (R–O)/$\sqrt{2}$ (Mn–O) determines the mismatch between the equilibrium bond length R–O and Mn–O of a $RMnO_3$ cubic perovskite. t is calculated from the empirical ionic radii [15,16]. Assuming that the introduction of Ce^{+4} converts Mn^{+3} to Mn^{+2}, we get the tolerance factor for $La_{0.7}Ce_{0.3}MnO_3$ = 0.89 and that for $Pr_{0.7}Ce_{0.3}MnO_3$ =

0.88. For a perfect size match (t = 1), the Mn–O–Mn bond angle (θ) is 180°. For t < 1, the MnO_6 octahedra tilt and rotate thereby decreasing θ less than 180° to adjust the excess space around the R-site. The partial replacement of R^{+3} ions by smaller Ce-ions increases the distortion of the ideal perovskite.

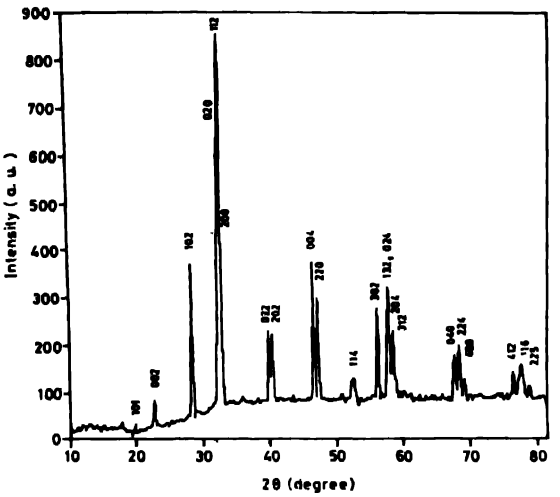

Figure 1. X-ray diffraction pattern of $La_{0.7}Ce_{0.3}MnO_3$ sample at room temperature.

The temperature dependence of resistivity and magnetoresistance of $La_{0.7}Ce_{0.3}MnO_3$ sample are shown in Figure 2. The temperature dependence of zero-field resistivity shows a sharp peak at 246 K and a broad peak at 220 K. The slow increase of resistivity with

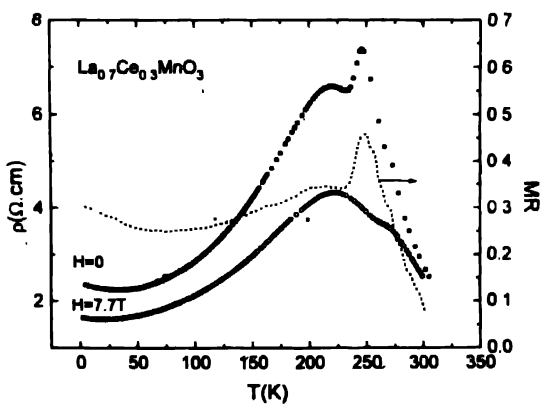

Figure 2. Temperature dependence of resistivity of $La_{0.7}Ce_{0.3}MnO_3$ at zero field and at 7.7 T alongwith the MR.

decreasing temperature in the low temperature region (T < 50 K) may originate from the weak localisation effect. Such phenomenon is very common in resistive samples. With the decrease of oxygen content conductivity decreases and these two peaks merge into a single broad peak. The effect of oxygen overdoping on resistive peaks has been investigated by annealing the same sample at 3 atmosphere of oxygen pressure at 900°C. With increasing oxygen content the conductivity increases, the second peak (broader one) becomes sharper

and the splitting between the two peaks is more prominent. X-ray diffraction pattern shows only the decrease of orthorhombicity with oxygen content but no secondary phase. Similar

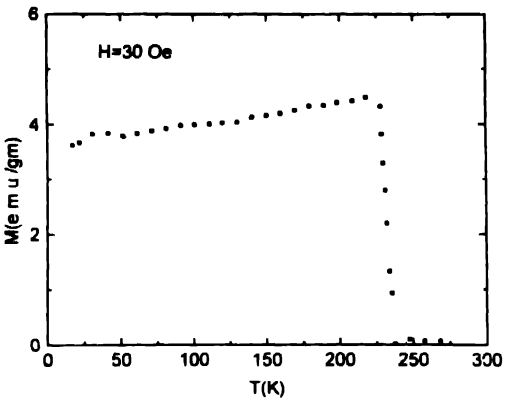

Figure 3. Magnetisation *versus* temperature curve for $La_{0.7}Ce_{0.3}MnO_3$ sample

behaviour has also been observed for overdoped $La_{2/3}Ba_{1/3}MnO_3$ sample [17]. Except in the vicinity of the peaks, the temperature dependence of resistivity at 7.7 T is similar to that of the zero-field one. The second peak does not change its position with the application of the magnetic field whereas the first peak shifts towards the higher temperature (270 K) and appears as a shoulder-like feature at 7.7 T. The difference in the nature of the field dependence of these two resistive peaks suggests that they may have different origins. The MR [= $(\rho(0) - \rho(H))/\rho(0)$, where $\rho(0)$ is the zero-field resistivity and $\rho(H)$ is the resistivity at 7.7 T] shows a sharp peak at 247 K which is very close to the temperature that corresponds to first peak position. The maximum value (46%) in MR is observed at this temperature. At low temperatures, MR increases slowly with the decrease in temperature which may be partly due to the suppression of weak localisation effect.

The temperature dependence of low-field magnetisation (M) for $La_{0.7}Ce_{0.3}MnO_3$ is shown in Figure 3. The sample was first cooled down to the lowest temperature in absence of any magnetic field and then the magnetisation was measured after switching on the field (30 Oe) and warming it slowly. M increases slowly with the increase of temperature up to 220 K and then falls sharply above this temperature. This indicates that a sharp FM to PM transition occurs at around 233 K (T_c, which is defined as the point of inflection in the M vs T curve). The temperature dependence of this low-field magnetisation of $La_{0.7}Ce_{0.3}MnO_3$ is similar to other systems [6]. We have also measured the magnetisation of $La_{0.7}Ce_{0.3}MnO_3$ sample at high fields [14]. At high magnetic fields, the T dependence of magnetisation is similar to that of conventional ferromagnet, *i.e.*, M increases with decreasing temperature and saturates at low temperature.

We have also measured the resistivity and magnetisation of $Pr_{0.7}Ce_{0.3}MnO_3$ and $Nd_{0.7}Ce_{0.3}MnO_3$ samples [14]. The resistivity of $Pr_{0.7}Ce_{0.3}MnO_3$ is very high and the temperature dependence of resistivity shows a peak at 104 K indicating a metal-insulator transition. The magnetisation *vs* temperature curve presents a smooth transition from ferromagnetic to paramagnetic state. The magnetoresistance reaches as high as 82.5%

at 7.7 T. $Nd_{0.7}Ce_{0.3}MnO_3$ sample also exhibits similar behaviour. But the resistivity is higher than that for Pr-based sample [14].

In conclusion, we have shown for the first time the GMR effect in Ce-doped manganite compounds. Our results show that MR is symmetric with respect to the presence of Mn^{+2} and Mn^{+4} ions provided in this system Ce exists in a tetravalent state or in a state having a valency intermediate between +3 and +4. Moreover, MR is very sensitive to oxygen content and new feature (two peaks) in the resistivity appears with oxygen overdoping in $La_{0.7}Ce_{0.3}MnO_3$. To know the exact valence state of Ce-ion and Mn-ions one should study the spectroscopic properties and microchemical analysis on these samples. Further studies in this regard are in progress.

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